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CHEMICAL ANALYSIS OF THE S-3 DISPOSAL PONDS (APRIL, 1978)

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August 11, 1978

UNION CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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OAK RIDGE Y-12 PLANT
P. O. Box Y, Oak Ridge, Tennessee 37830
Operated by
UNION CARBIDE CORPORATION, NUCLEAR DIVISION
for the
DEPARTMENT OF ENERGY, OAK RIDGE OPERATIONS

SUMMARY

Annual samples from the S-3 disposal pond were taken during April, 1978. A comparison of past S-3 pond sample data, as far back as 1961-62, was also made. Concentrations and total quantities of chemicals in the ponds have been significantly reduced since 1975 which is a result of the startup of the new acid waste recycle facility and a reduction in the amounts of pickling bath wastes discarded in the plant (Table 1). As an example, the total nitrate wastes in the ponds in 1975 was 2,019,000 kilograms and in 1978 the nitrate wastes had been reduced to 990,000 kilograms.

One of the four ponds, labeled S-E pond, is now being used to discard waste calcium carbonate and potassium hydroxide. The pH of the water has increased from a nominal 0.8 to 4.8, and a significant reduction in the amounts of chemicals which are insoluble at a pH of 4.8 has occurred (Table 2). As an example, the amount of soluble aluminum ions in the S-E pond has decreased from 12,000 to 1,100 kilograms.

Trace amounts of plutonium and neptunium ions are present in three of the four ponds. The S-E pond (pH 4.8) contains less than the detectable quantities of these elements. Calculations were made, assuming all of these radionuclides were precipitated in a 1-inch layer, and the activity of the 1-inch layer in soil would not present a disposal problem (Table 1).

INTRODUCTION

Prior to the successful startup of the biodenitrification and acid waste recycle facility,[1] considerable volumes of acidic raffinates and condensates were discharged to four open disposal ponds—collectively referred to as the S-3 disposal ponds. In prior years, these ponds had also been a "catchall" for smaller volumes of such effluents as waste acid plating solutions and rinse solutions. Current waste management practices have succeeded in limiting the quantity of acidic pollutants in these ponds. In addition, caustic wastes, mainly calcium carbonate and potassium hydroxide, have been added to neutralize the excess acid in one of the ponds. Samples of the four ponds have been taken to provide data pertaining to the chemical and nuclear composition of the soluble ions in the pond solutions. The main purpose of this report is to provide a consolidated historical record of monitoring data which should also be useful for comparative studies of the effectiveness of current or proposed new facilities/procedures on controlling waste discharged to the S-3 ponds.

PRIOR WORK BY Y-12

Previous years' samples were reported in earlier Y-12 Development Division Technical Progress Reports[2] and by internal correspondence.[3]

PRESENTATION OF EXPERIMENTAL WORK

Annual samples of the S-3 disposal ponds were taken during April, 1978. The ponds are located at the west end of the Y-12 Plant and have been designated as the Northeast, Southeast, Northwest, and Southwest ponds (Figure 1). Each disposal pond was sampled at the top and bottom to provide chemical, spectrochemical, and radioactivity data.

The top of each pond was sampled by skimming the top of the pond 1.5 meters from the shoreline at approximately the half-way point of the north shore for the two southern ponds and approximately the half-way point of the south shore for the two northern ponds.

To sample the bottom of each pond, a 6-inch-long by 2-inch-ID piece of pipe, capped at each end, was fabricated. Two 1/4-inch-diameter holes were drilled in one of the capped ends, thus the sampler was heavy enough to quickly sink to the pond bottom before the air could be displaced with the pond solution. The bottom of each pond was sampled at a distance of 9 meters from the half-way point of the north shore of the two southern ponds and at the same distance from the half-way point of the southern shore of the two northern ponds.

Table 1 data are calculated amounts of chemicals based on laboratory analyses taken in 1962, 1975, and 1978. Significant reductions in the amounts of nitrate ions have occurred as a result of the startup of the acid waste recycle facility ($\sim 2.0 \times 10^6$ kg in 1975 versus $\sim 1.0 \times 10^6$ kg in 1978). The amounts of soluble heavy metals in the ponds have also decreased due to a decrease in the amounts discarded from pickling baths in the plant and neutralization of one of the four ponds.

Table 1 data also report the calculated amounts of plutonium and neptunium in the ponds. Calculations also indicate that if these elements are precipitated into a 1-inch soil layer over an area of 40 x 40 feet in the bottom of each pond, the soil will have an activity of less than 10 nCi/gram which is considered to be a safe burial limit.

Table 2 presents comparative data on the S-E pond which is being neutralized by the addition of waste calcium carbonate and potassium hydroxide. The pH has increased from 0.8 in 1975 to 4.8 in 1978. No acid wastes have been added to this pond since 1975, except for unknown amounts of leakage from the adjacent ponds. The amounts of heavy metals in solution in this pond have sharply decreased due to precipitation at the increased pH level. An example is the soluble aluminum was 12,000 kilograms in 1975 and in 1978 only 1,100 kilograms remained in solution.

Table 3 provides a compilation of the chemical and spectrochemical analyses of the top and bottom of the four ponds. The as-received pH was determined for each sample. All samples were filtered, using 0.45 micrometer filter paper, for analyses of the aqueous portion. Chloride determination was made by the specific-ion electrode; fluoride was analyzed by pyrohydrolysis and the specific-ion electrode. Fluorometric mass spectrophotometry was used to determine the uranium concentration; uranium isotopes were determined

by thermal emission assay. Nitrate concentrations were determined by ultraviolet analysis, while mercury and cadmium were determined by atomic absorption. The top and bottom of the Southeast pond were not analyzed for nonuranium actinides due to the large quantity of samples required for analyses (low concentrations of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{237}Np.

As previously stated, the Southeast pond is being used as a disposal basin for biodenitrification sludge (mainly calcium carbonate) and a potassium hydroxide-potassium fluoride slurry from the hydrogen fluoride scrubbers. As can be seen from Table 3, these chemicals have caused a marked increase in the pond pH as the pond is neutralized. Also, metals, such as aluminum and uranium, are lower in the aqueous sample, due to their being precipitated as the pH rises.

Table 4 gives a compilation of the radioactivity associated with the S-3 disposal ponds. These data show that the radionuclide concentration in the ponds are very low. Table 5 reports an isotopic analysis of the uranium found in each pond and reveals that the isotopic assay of the uranium is basically 99.6% ^{238}U. No prior data are available for comparison.

FUTURE WORK

The S-3 disposal pond will be sampled on a yearly basis and a comparison with data from prior years' samples will be made.

REFERENCES

1. Francke, H. C.; Conversion of Acidic Nitrate Effluents to Fertilizers and Applications to Forested Lands, Y/DA-4975; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee (1972).

2. Y-12 Development Division Technical Progress Report, Y-1333-A, p A-13; February 1, 1962.

3. Chemical Compositions of S-3 Ponds; Internal Correspondence, J. M. Napier, February 6, 1976.

Table 1

CHEMICALS IN S-3 PONDS
(Solution)

	Kilograms		
	1962	1975	1978
NO_3^-	2,267,000	2,019,000	990,000
U	-	13,165	5,000
F^-	22,170	16,700	400
Th	-	3,400	1,300
Al	--	146,100	55,200
Ca	-	18,700	28,000
Mg	--	16,500	9,800
Cl^-	2655	9,300	36,000
Cr	-	-	860
Cu	-	-	500
Fe	-	-	12,100
K	-	-	5,300
Na	-	-	56,100
Ni	-	-	1,600
^{238}Pu	-	0.0623 gm	0.001 gm(1)
^{239}Pu	-	0.210 gm	0.0116 gm(2)
^{237}Np	-	-	75 gm(3)

NOTE: If it is assumed that of the Pu and Np is deposited in a 1-inch soil layer over an area of 40 x 40 ft, the average soil activity would be:

(1) ^{238}Pu — 0.1 nCi/g of dry soil

(2) ^{239}Pu — 0.04 nCi/g of dry soil

(3) Np — 3.00 nCi/g of dry soil

A limit of 10 µCi/g soil is acceptable.

Table 2

COMPARATIVE DATA ON SE POND

	Kilogram	
	1975	1978
pH	0.8	4.8
NO_3^-	155,300	67,500
U	340	75
F^-	1,125	32
Th	260	1
Al	12,000	1,100
Ca	1,600	16,600
Mg	1,400	1,180
Cl^-	750	1,800
^{238}Pu	0.0037 gm	(1)
^{239}Pu	-	(1)
^{237}Np	-	(1)

(1) Values less than detectable amounts.

Table 3

SPECTROGRAPHIC AND CHEMICAL ANALYSES OF THE S-3 DISPOSAL PONDS

	Southeast Pond		Northeast Pond		Southwest Pond		Northwest Pond	
Test	Top (mg/dm^3)	Bottom (mg/dm^3)	Top (mg/dm^3)	Bottom (mg/dm^3)	Top (mg/dm^3)	Bottom (mg/dm^3)	Top (mg/dm^3)	Bottom (mg/dm
pH	4.2	5.3	1.2	0.8	1.4	1.2	1.1	0.8
Cl^-	207	286	2330	1641	687	789	1600	1003
F^-	9	1	9	25	5	4	8	31
NO_3^-	7,590	10,410	17,840	73,840	11,020	20,460	21,560	69,100
U	17.51	3.24	139.57	316.57	80.34	111.21	180.81	313.13
Ag	< 0.1	< 0.1	0.6	1.8	0.2	0.4	0.5	1.8
Al	300	8.5	1202	4522	668	1370	1346	4858
As	0.001	0.003	0.028	0.115	0.013	0.025	0.028	0.073
B	2.6	1.6	30	17	8.5	7.1	21	8.1
Ba	0.8	0.5	0.4	0.7	0.3	0.7	0.5	4.4
Ca	1,381	3,053	267	877	137	250	276	840
Cd	0.3	0.7	0.7	158	0.4	2.0	0.8	5.4
Co	0.2	0.4	0.5	1.1	0.4	0.5	0.5	1.4
Cr	8.5	< 0.1	60	37	11.9	11.6	43	34
Cu	3.9	0.3	13.2	44	6.0	10.5	12.8	32
Fe	0.8	1.8	168	765	88	347	174	1208
Hg	0.004	0.003	0.052	0.320	0.032	0.064	0.062	0.240
K	93	98	90	310	43	109	86	416
Li	5.1	6.9	12	32	4.1	7.9	9.5	25
Mg	125	190	169	654	99	199	198	672
Mn	8.3	12	7.5	24	5.2	11	9.1	22
Na	652	664	3475	2300	1234	1262	2617	1128
Ni	16	39	55	128	22	31	47	50
P	1.0	< 0.1	59	101	21	27	49	70
Se	0.005	0.002	0.018	0.003	0.029	0.022	0.033	0.009
Si	< 1.0	< 1.0	32	70	< 1	51	33	94
Sr	1.2	1.1	1.0	3.7	0.6	1.2	1.2	4.9

Table 3 (Cont'd)

SPECTROGRAPHIC AND CHEMICAL ANALYSES OF THE S-3 DISPOSAL PONDS

	Southeast Pond		Northeast Pond		Southwest Pond		Northwest Pond	
Test	Top (mg/dm^3)	Bottom (mg/dm^3)	Top (mg/dm^3)	Bottom (mg/dm^3)	Top (mg/dm^3)	Bottom (mg/dm^3)	Top (mg/dm^3)	Bottom (mg/dm^3)
Th	0.2	0.1	20	85	13	28	26	118
Ti	< 0.1	< 0.1	2.0	6.4	1.0	1.4	2.2	7.0
Y	< 0.1	< 0.1	< 0.1	0.3	< 0.1	< 0.1	0.1	0.2
Zn	1.9	1.4	8.5	12	2.2	4.0	5.6	10
Zr	< 0.1	< 0.1	2.0	8.0	1.2	2.7	2.5	11

Table 4

ACTIVITY ANALYSES OF THE S-3 DISPOSAL PONDS

Activity of Actinides	Southeast Pond		Northeast Pond		Southwest Pond		Northwest Pond	
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
Alpha								
$^{238, 239, 240}Pu$ (μCi/g U)	-	-	0.001	0.004	0.002	0.025	0.002	0.004
^{237}Np (μCi/g U)	-	-	0.003	0.013	0.012	0.010	0.012	0.013
^{232}U (d/min/μg U)	0.01	0.02	0.01	< 0.01	0.02	0.01	0.05	0.01
Total U Alpha[1] (d/min/μg U)	1.32	1.18	1.04	1.04	1.05	1.32	1.32	1.04
^{238}Pu (g/ℓ)	-	-	6.2×10^{-12}	6.7×10^{-11}	9.6×10^{-12}	1.1×10^{-11}	7.2×10^{-11}	6.1×10^{-11}
^{239}Pu (g/ℓ)	-	-	5.5×10^{-11}	7.0×10^{-10}	1.4×10^{-10}	1.2×10^{-10}	2.7×10^{-10}	1.3×10^{-10}
^{237}Np (g/ℓ)	-	-	6.0×10^{-7}	5.9×10^{-6}	1.3×10^{-6}	1.6×10^{-6}	3.0×10^{-6}	5.1×10^{-6}
Beta								
Ratio[2]	1.74	-	0.41	0.68	0.37	0.50	0.34	0.60
^{99}Tc (μCi/ml)	-	-	8.4×10^{-4}	9.1×10^{-5}	8.8×10^{-6}	3.1×10^{-5}	1.3×10^{-4}	10^{-6}
Gamma								
^{137}Cs (μCi/g U)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
^{99}Zr-Nb (μCi/g U)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
^{106}Ru (μCi/g U)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Others (μCi/g U)	None	None	None	None	None	None	None	None
Total Gamma (μCi/g U)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Total Gamma[3] (μCi/g U)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

[1] Calculated from isotopic abundances.

[2] Uranium enriched in ^{235}U to 93%. (No transuranics or fission products present.)

[3] $\frac{\text{Activity of Sample}}{\text{Activity of Uranium Standard}}$

Table 5

URANIUM ISOTOPIC ANALYSIS OF THE S-3 DISPOSAL POND

	Assay (Weight Percent)							
	Northeast Pond		Southeast Pond		Northwest Pond		Southwest Pond	
Nuclide	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
^{234}U	0.002	0.002	0.004	0.003	0.004	0.002	0.002	0.004
^{235}U	0.308	0.297	0.323	0.315	0.315	0.298	0.333	0.321
^{236}U	0.014	0.008	0.014	0.010	0.015	0.012	0.016	0.017
^{238}U	99.676	99.693	99.659	99.672	99.666	99.688	99.649	99.658

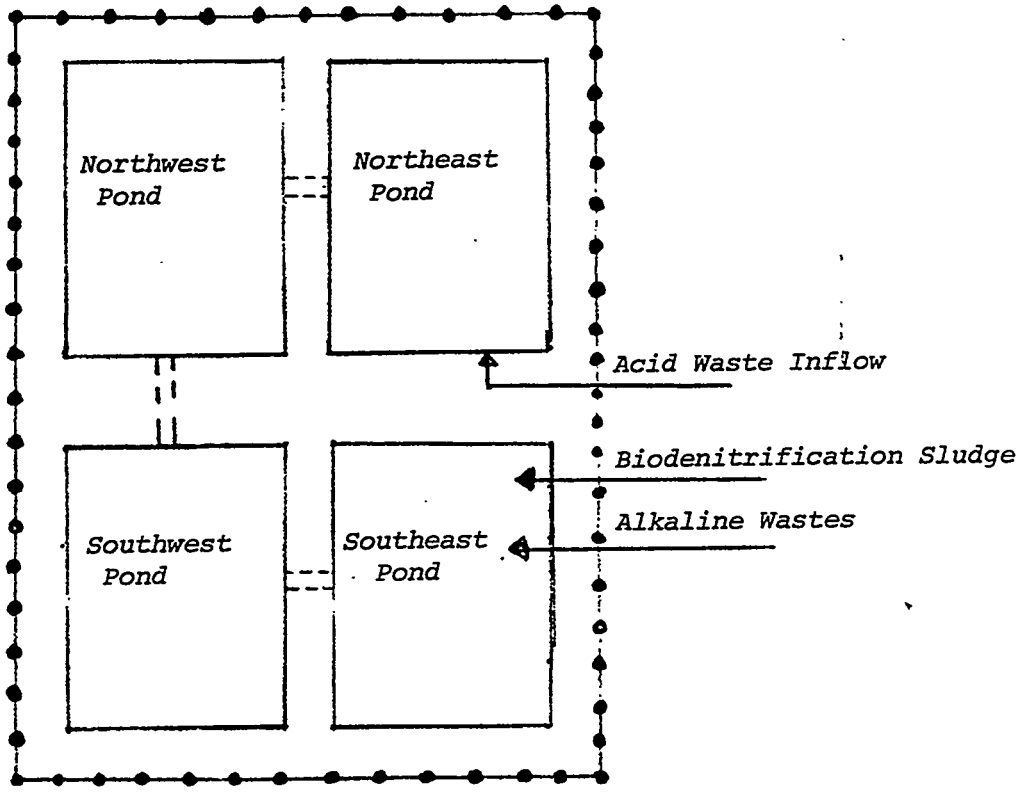

Figure 1. ENTRANCE OF WASTE SOLUTIONS TO THE DISPOSAL PONDS.

Estimated Pond Volumes:

Northwest — 9.46×10^6 liters (2.5×10^6 gallons)

Northeast — 7.5×10^6 liters (2.0×10^6 gallons)

Southwest — 9.46×10^6 liters (2.5×10^6 gallons)

Southeast — 7.5×10^6 liters (2.0×10^6 gallons)

Distribution:

H. K. Bailey
D. J. Bostock
O. W. Briscoe
R. B. Burditt
W. H. Dodson/J. M. Googin
I. W. Jeter
R. G. Jordan
A. Keith
H. T. Kite
G. B. Marrow
J. D. McLendon
J. M. Napier
J. Parsons
L. R. Phillips
M. Sanders
J. M. Schreyer
H. F. Smith, Jr.
R. D. Smith
H. H. Stoner
J. W. Strohecker
R. D. Williams
W. J. Yaggi
Y-12 Central Files (Y-12RC)